Ligand Substitution on (*N,N*-Dimethylformamide)[2,2′,2″-tri(*N,N*-dimethylamino)triethylamine]cobalt(II)

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The selectivity exhibited by $[Co(hmtren)(dmf)]^{2+}$ [hmtren = $N(CH_2CH_2NMe_2)_3$, dmf = $HCONMe_2$] for substitution of dmf by NCS^-, N_3^-, and Br^-, and the observed ligand-substitution rate laws are consistent with the operation of an I_a mechanism. This contrasts with an earlier observation that $[Cu(hmtren)(dmf)]^{2+}$ undergoes ligand substitution through an I_d mechanism. These new data support the argument, adduced previously from dmf exchange studies, that the tendency for ligand substitution in the $[M(hmtren)(dmf)]^{2+}$ species (M = first-row transition metal) to occur through an associative (a) activation mode increases as the electronic occupancy of the *d* orbitals decreases.

The activation volumes ($\Delta V^‡$) for *N,N*-dimethylformamide (dmf) exchange on $[M(hmtren)(dmf)]^{2+}$ [where hmtren = 2,2′,2″-tri(*N,N*-dimethylamino)triethylamine] are −6, −2.71, and +6.5 cm^3 mol^{-1} respectively when M = Mn, Co, and Cu consistent with the operation of I_a dmf exchange mechanisms in the first two cases and an I_d mechanism for the last.[1] This increasing tendency for solvent exchange to occur through an associative (a) activation mode as the electronic occupancy of the *d* orbitals decreases is also observed for the first-row transition-metal series $[M(solvent)_6]^{2+}$ for which $\Delta V^‡$ data indicate that when M = V and Mn an I_a mechanism operates and that when M = Fe, Co, and Ni an I_d mechanism operates.[2] These observations indicate that the transfer of cobalt(II) from the $[Co(dmf)_6]^{2+}$ environment to that of $[Co(hmtren)(dmf)]^{2+}$ engenders a change from an I_d to an I_a mechanism. The latter mechanism is unusual for cobalt(II) and should result in $[Co(hmtren)(dmf)]^{2+}$ exhibiting a significant selectivity for X^- ligands substituting dmf in contrast to $[Cu(hmtren)(dmf)]^{2+}$ which as a consequence of its I_d mechanism exhibits a negligible selectivity.[3]

Experimental

The salt $[Co(hmtren)(dmf)][ClO_4]_2$, for which excellent analyses were obtained, was prepared in a similar manner to the copper(II) analogue.[3] **CAUTION**: *Perchlorate salts of metal complexes may be explosive and should be handled with caution. No explosion hazard was encountered in this study.* All other reagents were purified and handled as previously described.[3] In the presence of oxygen, dmf solutions of $[Co(hmtren)(dmf)][ClO_4]_2$ slowly darken, probably as a consequence of the formation of a μ-peroxo-species. Accordingly, care was taken to minimise exposure to oxygen and only solutions freshly prepared under anhydrous conditions in a dry high-purity nitrogen-flushed glove-box were used in equilibrium and kinetic studies. Stoicheiometric studies of the species formed between $[Co(hmtren)(dmf)]^{2+}$ and X^- (= NCS^-, N_3^-, or Br^-) using Job's method[4] and stopped-flow spectrophotometric ligand-substitution studies were carried out using equipment and methods previously described, as was the data handling and treatment.[3] The observation wavelengths were 312 nm (NCS^- system), 322 nm (N_3^- system), and 525 and 615 nm (Br^- system). For the Job's method studies the $[Co(hmtren)(dmf)^{2+}]$ ranges were: 5.2×10^{-4}—4.7×10^{-3}, for $[Br^-] = 5.3 \times 10^{-4}$—$4.8 \times 10^{-3}$; 1.2×10^{-4}—1.1×10^{-3}, for $[N_3^-] = 1.3 \times 10^{-3}$—$1.2 \times 10^{-4}$; 7.6×10^{-5}—6.0×10^{-4}, for $[NCS^-] = 7.3 \times 10^{-5}$—$6.4 \times 10^{-4}$ mol dm^{-3}. For the stopped-flow spectrophotometric studies the initial $[Co(hmtren)(dmf)^{2+}]$ ranges were (0.04739—1.144) × 10^{-3} in the presence of NCS^- [(0.05649—3.036) × 10^{-2}], (0.2207—3.456) × 10^{-4} in the presence of N_3^- [(0.5018—6.141) × 10^{-3}], and (0.9282—1.392) × 10^{-3} mol dm^{-3} in the presence of Br^- [(1.512—7.928) × 10^{-2} mol dm^{-3}]; in all cases $[X^-]$ was in at least 17-fold excess over $[Co(hmtren)(dmf)^{2+}]$. In all solutions the ionic strength was adjusted to 0.50 mol dm^{-3} with $NaClO_4$.

Results

Using Job's method,[4] dmf was shown to be substituted in $[Co(hmtren)(dmf)]^{2+}$ by NCS^-, N_3^-, and Br^- to form 1:1 species characterised by apparent stability constants *ca.* 10^3 dm^3 mol^{-1} at 298.2 K. The spectra of $[Co(hmtren)(dmf)]^{2+}$ and its NCS^-, N_3^-, and Br^- analogues are shown in Figure 1. Substitution of dmf by Cl^- also occurs but the resultant spectral changes were insufficient for accurate stopped-flow spectrophotometric measurements and this system was not studied further. The variations of the first-order rate constant for the approach to equilibrium, $k_{obs.}$ (determined by stopped-flow spectrophotometry), with the total substituting concentration of ligand, $[X^-]$, are shown in Figure 2 for $X^- = NCS^-$ and N_3^- and in Figure 3 for $X^- = Br^-$. A combination of the moderate magnitude of the spectral change accompanying ligand substitution and the instrumental dead time (*ca.* 2 ms) caused the experimental error to increase substantially for $k_{obs.} > 300$ s^{-1} and consequently limited the $[X^-]$ range studied when $X^- = NCS^-$ and N_3^-. The spectral change characterising the Br^- system is quite small and in consequence it was necessary to work at a greater $[Co(hmtren)(dmf)^{2+}]$ than was the case for the NCS^- and N_3^- systems. In order to maintain pseudo-first-order kinetic conditions, the lowest $[Br^-]$ studied was 1.512×10^{-2} mol dm^{-3}, but the small $k_{obs.}$ values permitted studies at a higher $[Br^-]$ than the $[NCS^-]$ and $[N_3^-]$ studied (see Experimental section).

Discussion

The variations of $k_{obs.}$ with $[X^-]$ in Figures 2 and 3 are consistent with rate equation (1) which characterises the ligand-substitution interchange mechanism[5] (2) for which K_0 is the formation constant of the encounter complex $[Co(hmtren)(dmf)]^{2+}\cdots X^-$ in which X^- resides in the second co-

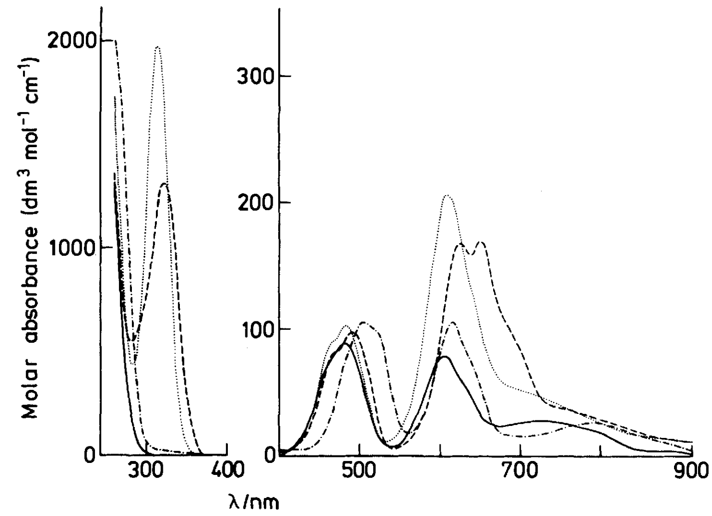

Figure 1. Ultraviolet–visible absorption spectra of $[Co(hmtren)(dmf)]^{2+}$ (———) and $[Co(hmtren)X]^+·X^-$ = NCS^- (· · · ·), N_3^- (– – – – –), or Br^- (– • – • – •) in dmf

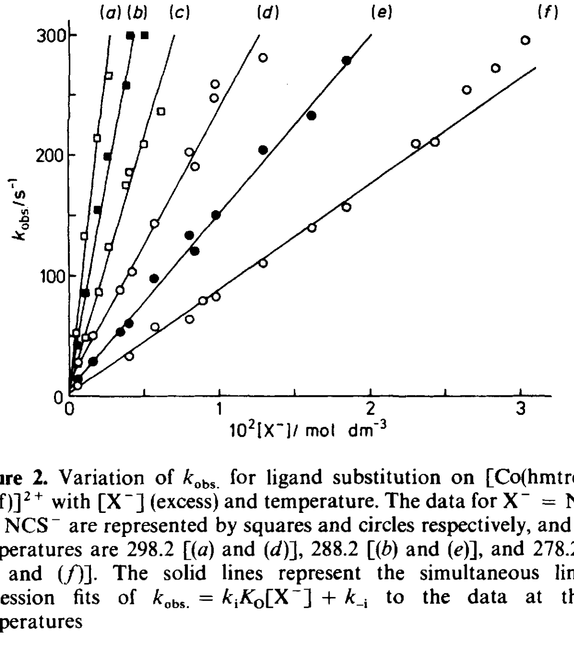

Figure 2. Variation of $k_{obs.}$ for ligand substitution on $[Co(hmtren)(dmf)]^{2+}$ with $[X^-]$ (excess) and temperature. The data for $X^- = N_3^-$ and NCS^- are represented by squares and circles respectively, and the temperatures are 298.2 [(*a*) and (*d*)], 288.2 [(*b*) and (*e*)], and 278.2 K [(*c*) and (*f*)]. The solid lines represent the simultaneous linear regression fits of $k_{obs.} = k_iK_O[X^-] + k_{-i}$ to the data at three temperatures

$$k_{obs.} = \{k_iK_O[X^-]/(1 + K_O[X^-])\} + k_{-i} \quad (1)$$

$$[Co(hmtren)(dmf)]^{2+} + X^- \underset{fast}{\overset{K_O}{\rightleftharpoons}} [Co(hmtren)(dmf)]^{2+} \cdots X^- \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} [Co(hmtren)X]^+ \cdots dmf \quad (2)$$

ordination sphere of $[Co(hmtren)(dmf)]^{2+}$, and k_i and k_{-i} respectively represent the rate-determining interchange of X^- between the second and first co-ordination spheres of the encounter complex and *vice versa*. The $k_{obs.}$ data for NCS^- and N_3^- are consistent with a first limiting condition $K_O[X^-] \ll 1$ such that equation (1) reduces to $k_{obs.} \approx k_iK_O[X^-] + k_{-i}$ and the linear regression lines for the simultaneous fit of the NCS^- system at the three experimental temperatures are shown in Figure 2, as are those for the N_3^- system. The derived k_iK_O values appear in the Table but the k_{-i} values are negligible within experimental error and are not further discussed. The k_iK_O values for N_3^- are substantially greater than those for NCS^- but it cannot be determined from the available data whether this is a consequence of differences in k_i, K_O, or both parameters. By assuming values for K_O (the upper limit of which is set at that which introduces a substantial deviation from a linear dependence of $k_{obs.}$ on $[X^-]$ over the experimental $[X^-]$ range) a range of k_i values may be derived as shown in the Table.

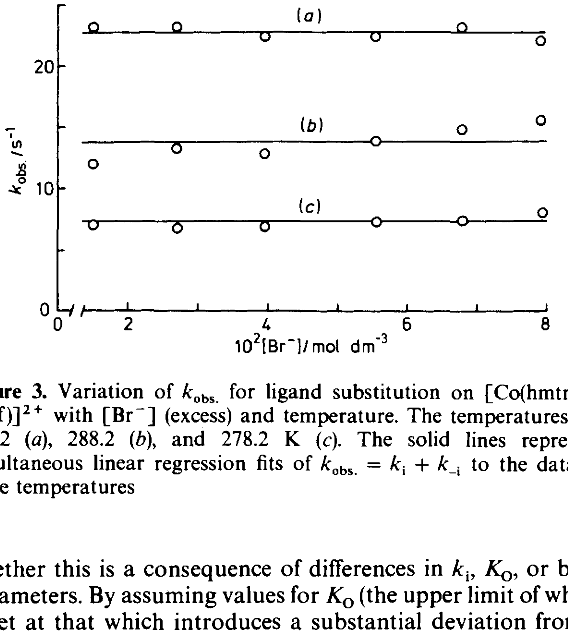

Figure 3. Variation of $k_{obs.}$ for ligand substitution on $[Co(hmtren)(dmf)]^{2+}$ with $[Br^-]$ (excess) and temperature. The temperatures are 298.2 (*a*), 288.2 (*b*), and 278.2 K (*c*). The solid lines represent simultaneous linear regression fits of $k_{obs.} = k_i + k_{-i}$ to the data at three temperatures

The invariance of $k_{obs.}$ with $[Br^-]$ (Figure 3) is consistent with a second set of limiting conditions $K_O[X^-] \gg 1$ such that equation (1) reduces to $k_{obs.} = k_i + k_{-1}$. It was noted earlier that the overall apparent equilibrium constant for the ligand-substitution process is *ca.* 10^3 dm^3 mol^{-1}, and hence $k_{obs.} \approx k_i$. The k_i values derived from a simultaneous linear regression fit of the $k_{obs.} = k_i + k_{-i}$ to the data at the three experimental temperatures and the associated activation parameters appear in the Table. Within the scatter of the experimental $k_{obs.}$ data, K_O values in the range 200—400 dm^3 mol^{-1} would produce the invariance of $k_{obs.}$ with $[Br^-]$. Such K_O values fall within the 52—464 dm^3 mol^{-1} range indirectly determined for the ligand substitution of $[Cu(hmtren)(dmf)]^{2+}$ by NCS^-, N_3^-, and Br^- for which the full $k_{obs.}$ variation with $[X^-]$ predicted by equation (1) was observed.[3] {The Fuoss equation[6] predicts K_O = 101 dm^3 mol^{-1} for $[Co(hmtren)(dmf)]^{2+}$ and X^- considered as spheres at an interaction distance = 56.5 pm and for a dielectric constant = 36.7, but the applicability of this equation

Table. Data for ligand substitution of $[M(hmtren)(dmf)]^{2+}$ by X^-

X^-	$10^3 k_i K_O$ [a]/ $dm^3\ mol^{-1}\ s^{-1}$	T/K	K_O [b]/ $dm^3\ mol^{-1}$	k_i [c]/s^{-1}
(*i*) $[Co(hmtren)(dmf)]^{2+}$ system				
NCS^-	22.4 ± 0.7	298.2	50	448
	22.4 ± 0.7	298.2	100	224
	14.6 ± 0.4	288.2		
	8.68 ± 0.19	278.2		
N_3^-	111 ± 9	298.2	50	2 220
	111 ± 9	298.2	100	1 110
	111 ± 9	298.2	200	555
	67.2 ± 3.6	288.2		
	41.9 ± 2.0	278.2		
Br^-		298.2		23.1 ± 0.6 [d]
		288.2		13.2 ± 0.3
		278.2		7.23 ± 0.19
dmf [e]		298.2		51.4 ± 4.2
(*ii*) $[Cu(hmtren)(dmf)]^{2+}$ system [f]				
NCS^-		298.2	175 ± 15	529 ± 32
N_3^-		298.2	464 ± 15	435 ± 19
Br^-		298.2	52 ± 3	563 ± 27
dmf		298.2		555 ± 39

[a] Errors represent one standard deviation for simultaneous fit of $k_{obs.} = k_i K_O[X^-] + k_{-i}$ to data at three temperatures assuming an Eyring-type temperature dependence of $k_i K_O$. [b] Assumed values for M = Co; derived values for M = Cu. [c] Derived using assumed K_O when M = Co and $X^- = NCS^-$ and N_3^-. In all other cases k_i is directly determined. [d] Derived through a simultaneous fit of $k_{obs.} = k_i + k_{-i}$ to $k_{obs.}$ data at three temperatures assuming the Eyring relationship; $\Delta H^\ddagger = 38.2 \pm 1.5$ kJ mol^{-1} and $\Delta S^\ddagger = -90.5 \pm 5.2$ J K^{-1} mol^{-1} where the errors for these parameters and $k_{obs.}$ represent one standard deviation. [e] Data from ref. 1. [f] Data from ref. 3.

to species as large as $[Co(hmtren)(dmf)]^{2+}$ and the appropriate value of the dielectric constant are in some doubt.}

It is seen from the Table that k_i characterising the substitution of dmf by Br^- in $[Co(hmtren)(dmf)]^{2+}$ is substantially less than k_i characterising substitution by N_3^- and NCS^- despite the fact that precise k_i values for the latter two species cannot be determined from the present experimental data as discussed earlier. This is consistent with the operation of an I_a ligand-substitution mechanism for $[Co(hmtren)(dmf)]^{2+}$. {It is notable that for ligand substitution on $[Cr(dmf)_6]^{3+}$, which also proceeds through an I_a mechanism, k_i increases[7] in the sequence $Br^- <$ dmf $< NCS^- < N_3^-$, a similar pattern to that observed in this study.} In contrast k_i shows only a small variation with the nature of X^- for $[Cu(hmtren)(dmf)]^{2+}$ (Table) which undergoes ligand substitution through an I_d mechanism. As neither $[Co(hmtren)(dmf)]^{2+}$ nor its copper(II) analogue is sufficiently substitution labile for selectivity for the entering group to be decreased,[8] it is clear that these ligand-substitution data support the earlier mechanistic assignments made on the basis of $\Delta V^\ddagger$ data.[1] The operation of an associative activation mode for $[Co(hmtren)(dmf)]^{2+}$ in contrast to the dissociative in $[Co(dmf)_6]^{2+}$ is probably a consequence of the lower co-ordination number of the first species and hence its enhanced ability to form a new bond in the transition state, whereas in the case of $[Cu(hmtren)(dmf)]^{2+}$ the greater electronic occupancy of the *d* orbitals is probably the dominant factor favouring a dissociative activation mode.

Acknowledgements

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